

Dynamics of complex-forming bimolecular reactions

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The presentation is about a theoretical reaction dynamics study on the reaction of H atoms with ground-state triplet or excited-state singlet O₂ molecules, which is the most important chain-branching reaction in combustion. We used the quasiclassical trajectory (QCT) method on accurate potential energy surfaces (PES). Both reactions go through a deep potential well but on the singlet surface there is a barrier in the entrance channel, the triplet surface is barrierless. One purpose was the calculation of the thermal rate coefficient of the H atom + singlet O₂ reaction, which we found very large; larger than that of the H + triplet O₂ reaction even above 3000 K. The other purpose was the investigation of the parameters characterizing the dynamics of the reaction in order to understand which properties of the PES can be assigned to what kind of outcome. For the excited-state reaction, the repulsive wall of the deep well beyond the potential barrier caused the majority of reactions passing the barrier from the reactant side to return without reaction, indicating that Transition State Theory cannot be applied to this reaction. The motion of the atoms in the potential well of either the singlet or the triplet PES was found to be non-statistical. In addition, lifetime-, angular- and product state distributions were analyzed and connected to mass effects or the shape of the PES.

More details can be found in the papers

P. Szabó, G. Lendvay, A Quasiclassical Trajectory Study of the Reaction of H Atoms with O₂(¹Δ_g), J. Phys. Chem. A **119**, 7180–7189 (2015)

DOI: 10.1021/jp510202r

P. Szabó, G. Lendvay, Dynamics of Complex-Forming Bimolecular Reactions: A Comparative Theoretical Study of the Reactions of H Atoms with O₂(³Σ_g⁻) and O₂(¹Δ_g), J. Phys. Chem. A **119**, 12485–12497 (2015)

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The research of György Lendvay concentrates on theoretical studies of the dynamics, kinetics and mechanism of chemical reactions. In dynamics calculations, in addition to QCT calculations on reactions of polyatomic molecules such as the CH₃ + HBr → CH₄ + Br, methodological issues of QCT studies are addressed. The subject of reaction kinetics/mechanism investigations include mostly radical-molecule reactions, most recently involving compounds derived from biomass and extend to the structure and operation of transition-metal catalysts as well as of metalloporphyrins.